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Soliton excitations in deoxyribonucleic acid (DNA) double helices

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Dynamical theory of soliton excitations in deoxyribonucleic acid (DNA) double helices has been studied by a revised Hamiltonian in which the dipole-dipole interaction and the dipole—induced-dipole interaction between two bases in a complementary base pair are taken into account in addition to the hydrogen-bond energy. The motion equations of bases are a set of coupled sine-Gordon equations. The soliton solutions of these equations are studied in detail and the results are compared with the experimental data in the H-D exchange measurements of DNA chains.

I. INTRODUCTION

Recently, the existence of open states in deoxyribonucleic acid (DNA) double helices has been demonstrated by the H-D exchange measurements.[1-3] Englander *et al.* suggested first a theory of soliton excitations as an explanation for such open states.[4] Later, Yomosa proposed a further soliton theory by using what amounts to be a dynamic plane base-rotator model.[5,6] Developing this ideal further, Takeno and Homma improved Yomosa's model by a different Hamiltonian.[7,8] It is believed that such studies are important in the sense that the soliton excitations may advance a new mechanism in the duplication of DNA and the transcription of messenger ribonucleic acid (mRNA).

According to the *B*-form DNA model proposed by Watson and Crick, the two polynucleotide strands forming a double helix are held together by hydrogen bonds. This fact explains why the above authors took account of the H-bond energy mainly in their Hamiltonians for the study of soliton excitations in *B*-form DNA. However, it is recognized that the binding energy of the helix could not arise solely from hydrogen bonds. For example, measurements of enthalpy change during helix-coil transitions yield much higher values than one would expect by assuming that this change is due to the breakage of H bonds alone. In addition to H bonds, one has to consider the dipole-dipole interaction, the dipole—induced-dipole interaction, and the dispersion interaction between two bases in a complementary base pair. According to the calculations of Devoe and Tinoco,[9] the dipole-dipole interaction is predominant among them. It is the purpose of this paper to study the influence of these interactions, mainly the dipole-dipole energy, to the soliton excitations in the *B*-form DNA double helix.

This paper is organized as follows. In Sec. II we introduce a model Hamiltonian by taking account of the dipole-dipole and dipole—induced-dipole energies in addition to the H-bond energy. In Sec. III the soliton solutions of the motion equations in the case of $\lambda=0$ are studied. In Sec. IV a perturbation method is used to solve the equations of motion in the general case. In Sec. V the phonon mode is studied. In Sec. VI the parameters in this theory are estimated and some discussions are given.

II. HAMILTONIAN AND EQUATIONS OF MOTION

The *B*-form DNA in the Watson-Crick model is a double helix which consists of two strands S and S'. Let the z axis be the screw axis. The plane of base pair is perpendicular to the z axis. Following Yomosa's plane base-rotator model, each base is depicted by an arrow, and complementary base pair are depicted by conjugated arrows directed inward. Let P_n, P_n' be the points where the nth base pair are attached to the strands S and S', respectively. Let φ_n (φ_n') be the angle between such an arrow and the line P_nP_n'; then the H-bond energy between two bases in nth complementary base pair may take the form

$$B[1-\cos(\varphi_n-\varphi_n')] , \tag{2.1}$$

where B is a parameter associated with the H bond energy. This form of H-bond energy was used by many authors listed above, and it is consistent with the Pople formula.[10] The *B*-form DNA corresponds to $\varphi_n=\varphi_n'\doteq 0$.

In the realistic *B*-form DNA the magnitude of the dipole moments for the bases adenine (A), thymine (T), guanine (G), and cytosine (C) is large. Let $\mathbf{u}_A$, $\mathbf{u}_T$, $\mathbf{u}_G$, and $\mathbf{u}_C$ be the dipole moments for the bases A, T, G, and C, respectively. Since each base is represented by an arrow, then the directions of these dipole moments are either in parallel or antiparallel with the base arrows. According to the calculations of Devoe and Tinoco,[9] the G-C dipoles attract while the A-T dipoles repel between the coplanar bases in a base pair. Therefore $\mathbf{u}_G$ and $\mathbf{u}_C$ are arranged in a form of head to tail, while $\mathbf{u}_A$ and $\mathbf{u}_T$ are in a form of head to head. This is roughly correct for the realistic DNA molecules.

The dipole-dipole interaction energy between two bases in nth coplanar base pair takes the form[11]

$$[\mathbf{u}_1\cdot\mathbf{u}_2-3(\mathbf{u}_1\cdot\mathbf{R})(\mathbf{u}_2\cdot\mathbf{R})/R^2]/R^3 , \tag{2.2}$$

where $\mathbf{u}_1$ and $\mathbf{u}_2$ are the dipole moments of the bases G and C or A and T, respectively, and R is the distance. Hereafter we shall assume a simplification: Take R as a constant. Then formula (2.2) reduces to

$$\beta[\cos(\varphi_n-\varphi_n')-3\cos\varphi_n\cos\varphi_n'] , \tag{2.3}$$

$$\beta = u_1 u_2 / R^3 . \tag{2.4}$$

In this manner the interaction energy of dipole—induced-dipole interaction between two bases in nth base pair may take the form[11]

$$-\lambda \cos\varphi_n - \lambda \cos\varphi'_n + \text{const} , \tag{2.5}$$

where λ is a coupling constant associated with the dipole—induced-dipole interaction energy.

The dispersion energy between two bases in nth base pair is φ_n or φ'_n independent by assuming the distance R to be constant.[11] Therefore it has no contribution to the equations of motion.

Combining formulas (2.1)—(2.5), the interstrand interaction energy in nth base pair may be written as

$$\begin{aligned} V(\varphi_n,\varphi'_n) = {} & B[1-\cos(\varphi_n-\varphi'_n)] + \lambda(1-\cos\varphi_n) \\ & + \lambda(1-\cos\varphi'_n) \\ & + \beta\{3(1-\cos\varphi_n \cos\varphi'_n) \\ & \quad - [1-\cos(\varphi_n-\varphi'_n)]\} , \end{aligned} \tag{2.6}$$

where the zero level of the energy is taken for the B-form DNA. Then the Hamiltonian of B-form DNA double helix to be studied in this paper is

$$\begin{aligned} H = \sum_n [& \tfrac{1}{2} I(\dot{\varphi}_n^2 + \dot{\varphi}'^2_n) + V(\varphi_n,\varphi'_n) \\ & + \tfrac{1}{2} S(\varphi_n - \varphi_{n-1})^2 + \tfrac{1}{2} S(\varphi'_n - \varphi'_{n-1})^2] , \end{aligned} \tag{2.7}$$

where I is the mean value of the moments of inertia of the bases for the rotation around the axes P and P' which pass through the points P_n, P'_n and are in parallel with z axis, respectively, S is a parameter associated with the stacking energy of DNA chains.

The equations of motion of bases are soon obtained from Eq. (2.7),

$$\begin{aligned} I\ddot{\varphi}_n = {} & -B \sin(\varphi_n - \varphi'_n) \\ & - \beta[3 \sin\varphi_n \cos\varphi'_n - \sin(\varphi_n - \varphi'_n)] \\ & - \lambda \sin\varphi_n + S(\varphi_{n+1} - 2\varphi_n + \varphi_{n-1}) , \end{aligned} \tag{2.8a}$$

$$\begin{aligned} I\ddot{\varphi}'_n = {} & B \sin(\varphi_n - \varphi'_n) \\ & - \beta[3 \cos\varphi_n \sin\varphi'_n + \sin(\varphi_n - \varphi'_n)] \\ & - \lambda \sin\varphi'_n + S(\varphi'_{n+1} - 2\varphi'_n + \varphi'_{n-1}) . \end{aligned} \tag{2.8b}$$

To solve Eqs. (2.8) we shall assume the continuum approximation

$$\varphi_n(t) \Longrightarrow \varphi(z,t), \quad \varphi'_n(t) \Longrightarrow \varphi'(z,t), \quad \sum_n \Longrightarrow \int \frac{1}{a} dz , \tag{2.9}$$

where a is the base-pair spacing, $a \simeq 3.4$ Å. Then Eqs. (2.8) reduce to

$$\begin{aligned} & Sa^2 \varphi_{zz} - I\varphi_{tt} \\ & \quad = B \sin(\varphi - \varphi') \\ & \qquad + \beta[3 \sin\varphi \cos\varphi' - \sin(\varphi - \varphi')] + \lambda \sin\varphi , \end{aligned} \tag{2.10a}$$

$$\begin{aligned} & Sa^2 \varphi'_{zz} - I\varphi'_{tt} \\ & \quad = -B \sin(\varphi - \varphi') \\ & \qquad + \beta[3 \sin\varphi' \cos\varphi + \sin(\varphi - \varphi')] + \lambda \sin\varphi' . \end{aligned} \tag{2.10b}$$

Introducing u and v such that

$$u = \varphi + \varphi', \quad v = \varphi - \varphi' , \tag{2.11}$$

or

$$\varphi = (u+v)/2, \quad \varphi' = (u-v)/2 , \tag{2.12}$$

we then obtain

$$\begin{aligned} & u_{zz} - (1/c_0^2) u_{tt} \\ & \quad = (1/l^2) \sin u + (2/d^2) \sin(u/2) \cos(v/2) , \end{aligned} \tag{2.13a}$$

$$\begin{aligned} & v_{zz} - (1/c_0^2) v_{tt} \\ & \quad = (Q/l^2) \sin v + (2/d^2) \sin(v/2) \cos(u/2) , \end{aligned} \tag{2.13b}$$

where

$$\begin{aligned} & c_0 = (S/I)^{1/2} a, \quad l = [S/(3\beta)]^{1/2} a, \\ & d = (s/\lambda)^{1/2} a, \quad Q = (2B+\beta)/(3\beta) . \end{aligned} \tag{2.14}$$

III. SOLITON SOLUTIONS IN THE CASE OF $\lambda = 0$

It is easy to see that

$$\varphi = \varphi' = 0 \tag{3.1}$$

is a solution of Eqs. (2.10) and (2.13). This solution corresponds to the ground state of B-form DNA.

In addition to the solution (3.1) it is difficult to obtain other solutions of Eqs. (2.10) and (2.13). Equation (2.13) may be called a set of coupled sine-Gordon equations which, to the knowledge of the author, probably cannot be solved exactly in a general case presently. An estimate of the parameters (see Sec. VI) shows that $\lambda \ll \beta$ or $d \gg l$ therefore we may solve Eqs. (2.13) in the general case by the perturbation method. To do this we have to study the unperturbed equations, i.e., $\lambda = 0$ in Eqs. (2.13); then we have

$$u_{zz} - (1/c_0^2) u_{tt} = (1/l^2) \sin u , \tag{3.2a}$$

$$v_{zz} - (1/c_0^2) v_{tt} = (Q/l^2) \sin v . \tag{3.2b}$$

The Eqs. (3.2) are two independent sine-Gordon equations. The N-soliton solution of sine-Gordon equations (3.2) may be obtained by the inverse method or Bäcklund transformation techniques.[12] At present we consider only the single soliton solution of Eqs. (3.2)

$$u_0^{\pm} = 4 \tan^{-1} \exp(\pm x) , \tag{3.3a}$$

$$v_0^{\pm} = 4 \tan^{-1} \exp(\pm \sqrt{Q} x) , \tag{3.3b}$$

$$\begin{aligned} & x = (\gamma/l)(\xi - \xi_0) , \\ & \xi = z - ct , \\ & \gamma = (1 - c^2/c_0^2)^{-1/2} , \end{aligned} \tag{3.3c}$$

where c is the velocity of the soliton.

Based on the solutions Eqs. (3.3), eight sets of solutions of Eqs. (2.10) are found in the case of $\lambda=0$:

$$\varphi_1=u_0^+/2+n\pi,\quad \varphi_1'=u_0^+/2-n\pi\ , \tag{3.4}$$

$$\varphi_2=u_0^-/2-n\pi,\quad \varphi_2'=u_0^-/2+n\pi\ , \tag{3.5}$$

$$\varphi_3=m\pi+v_0^+/2,\quad \varphi_3'=m\pi-v_0^+/2\ , \tag{3.6}$$

$$\varphi_4=m\pi-v_0^-/2,\quad \varphi_4'=m\pi+v_0^-/2\ , \tag{3.7}$$

$$\varphi_{1,1}^0=(u_0^++v_0^+)/2,\quad \varphi_{1,1}^{0'}=(u_0^+-v_0^+)/2\ , \tag{3.8}$$

$$\varphi_{1,2}^0=(u_0^++v_0^-)/2,\quad \varphi_{1,2}^{0'}=(u_0^+-v_0^-)/2\ , \tag{3.9}$$

$$\varphi_{2;1}^0=(u_0^--v_0^+)/2,\quad \varphi_{2,1}^{0'}=(u_0^-+v_0^+)/2\ , \tag{3.10}$$

$$\varphi_{2,2}^0=(u_0^--v_0^-)/2,\quad \varphi_{2,2}^{0'}=(u_0^-+v_0^-)/2\ , \tag{3.11}$$

where m and n are integers. We shall say $m=n=0$ hereafter. The solutions φ_i and φ_i' $(i=1,2,3,4)$ are π-kink or antikink solitons. The solutions $\varphi_{i,j}^0$ and $\varphi_{i,j}^{0'}$ $(i,j=1,2)$ are either 2π-kink (antikink) or special solitons. Let us take the special soliton $\varphi_{1,1}^{0'}$ as an example. From (3.3) and (3.8) we obtain

$$\varphi_{1,1}^{0'}=2\tan^{-1}\frac{e^x-e^{\sqrt{Q}x}}{1+e^{(\sqrt{Q}+1)x}}\ . \tag{3.12}$$

It is an odd function of x, and $\varphi_{1,1}^{0'}(\pm\infty)=0$. It has a maximum value M and a minimum $-M$. A simple numerical calculation gives

$$2M=27.9^\circ,\quad Q=2.1\ , \tag{3.13a}$$

$$2M=32.6^\circ,\quad Q=2.4\ , \tag{3.13b}$$

where the value of Q will be estimated in Sec. VI. That is to say, $\varphi_{1,1}^{0'}$ is a special soliton in which the base vibrates within a magnitude of 27.9° (32.6°). Note that

$$\varphi_{1,1}^0(0)=\varphi_{1,2}^0(0)=\varphi_{2,1}^{0'}(0)=\varphi_{2,2}^{0'}(0)=\pi\ , \tag{3.14a}$$

$$\varphi_{1,1}^{0'}(0)=\varphi_{1,2}^{0'}(0)=\varphi_{2,1}^0(0)=\varphi_{2,2}^0(0)=0\ . \tag{3.14b}$$

Denote the soliton energy associated with φ_i and φ_i' by E_i $(i=1,2,3,4)$, and $\varphi_{i,j}^0$ and $\varphi_{i,j}^{0'}$ by $E_{i,j}$ $(i,j=1,2)$, then it is easy to see that

$$E_1=E_2,\quad E_3=E_4,\quad E_{1,1}=E_{1,2}=E_{2,1}=E_{2,2}\ . \tag{3.15}$$

Substituting Eqs. (3.4)–(3.11) into Eqs. (2.7) and (2.9), we find

$$E_1{:}E_3{:}E_{1,1}=1{:}\sqrt{Q}{:}(\sqrt{Q}+1)\ , \tag{3.16}$$

where

$$E_1=4(3\beta S)^{1/2}\gamma\ . \tag{3.17}$$

IV. SOLITON SOLUTIONS IN THE CASE OF $\lambda\neq0$

The case of $\lambda\neq0$ will be divided into three parts for the convenience of discussion.

1. $\varphi=\varphi'$, $u=2\varphi$, $v=0$. In this case, Eqs. (2.13) reduce to a double sine-Gordon equation

$$\varphi_{zz}-(1/c_0^2)\varphi_{tt}=(1/d^2)[\sin\varphi+2\eta\sin(2\varphi)]\ , \tag{4.1}$$

where

$$\eta=3\beta/(4\lambda)>\tfrac{1}{4}\ . \tag{4.2}$$

One of the soliton solutions of Eq. (4.1) is[13]

$$\varphi=\varphi'$$
$$=2\tan^{-1}\{\tau(1+4\eta)^{-1/2}\operatorname{cosech}[(1+4\eta)^{1/2}y]\}\ , \tag{4.3}$$

where

$$y=(\gamma/d)(z-ct)\ , \tag{4.4}$$

and $\tau=1$ or -1 corresponding to the kink or antikink, respectively. The energy of soliton (4.3) is[13]

$$\epsilon_1=8(3\beta S)^{1/2}\gamma\{[1+1/(4\eta)]^{1/2}+\ln[(1+4\eta)^{1/2}+2\eta^{1/2}]/(4\eta)\}\ . \tag{4.5}$$

2. $\varphi=-\varphi'$, $u=0$, $v=2\varphi$. In this case, Eqs. (2.13) reduce to another double sine-Gordon equation

$$\varphi_{zz}-(1/c_0^2)\varphi_{tt}=(1/d^2)(\sin\varphi+2\eta'\sin2\varphi)\ , \tag{4.6}$$

where $\eta'=Q\eta$. The soliton solution is similar to that of Eq. (4.1)

$$\varphi=-\varphi'$$
$$=2\tan^{-1}\{\tau(1+4Q\eta)^{-1/2}\operatorname{cosech}[(1+4Q\eta)^{1/2}y]\}\ , \tag{4.7}$$

and the soliton energy is

$$\epsilon_2=8[(2B+\beta)S]^{1/2}\gamma\{[1+1/(4Q\eta)]^{1/2}+\ln[(1+4Q\eta)^{1/2}+2(Q\eta)^{1/2}]/(4Q\eta)\}\ . \tag{4.8}$$

Note that

$$\lim_{\lambda\to0}\epsilon_2/\epsilon_1=\sqrt{Q}\ . \tag{4.9}$$

3. $|\phi|\neq|\varphi'|, u\neq0, v\neq0$. In this case, Eqs. (2.13) reduce to

$$u_{zz}-(1/c_0^2)u_{tt}=(1/l^2)[\sin u+\epsilon\sin(u/2)\cos(v/2)]\ , \tag{4.10a}$$

$$v_{zz}-(1/c_0^2)v_{tt}=(1/l^2)[Q\sin v+\epsilon\sin(v/2)\cos(u/2)]\ , \tag{4.10b}$$

where $\epsilon=1/(2\eta)$. An estimate of ϵ below gives the result $\epsilon=0.068$. Therefore it is reasonable to expand the solutions of Eqs. (4.10) into the form as

$$u=u_0+\epsilon u^{(1)}+O(\epsilon^2)\ , \tag{4.11a}$$

$$v=v_0+\epsilon v^{(1)}+O(\epsilon^2)\ , \tag{4.11b}$$

where u_0 and v_0 are the soliton solutions of the unperturbed Eqs. (3.2)

$$u_0=4\tan^{-1}\exp(\tau_1x)\ , \tag{4.12a}$$

$$v_0=4\tan^{-1}\exp(\tau_2\sqrt{Q}x)\ , \tag{4.12b}$$

where $\tau_1,\tau_2=1$ or -1 corresponds to the kink or antikink soliton, respectively. There are four combinations for

(τ_1,τ_2), i.e., (1,1); (1, −1); (−1,1); (−1, −1), which corresponds to four different solutions of Eqs. (4.10). Denote the solutions by $u_{i,j}$ and $v_{i,j}$ $(i,j=1,2)$, where $i,j=1$ as $\tau_1,\tau_2=1$; and $i,j=2$ as $\tau_1,\tau_2=-1$. We assume that $u^{(1)}$ and $v^{(1)}$ are still solitary wave or soliton having the same velocity c as soliton u_0 and v_0. Then substituting Eqs. (4.11) and (4.12) into Eqs. (4.10), we find

$$u^{(1)}_{i,j,xx}=(2\tanh^2 x-1)u^{(1)}_{i,j}+(-1)^j \operatorname{sech}x \tanh(\sqrt{Q}x) , \tag{4.13a}$$

$$\begin{aligned} v^{(1)}_{i,j,xx}=&Q[2\tanh^2(\sqrt{Q}x)-1]v^{(1)}_{i,j}\\ &+(-1)^i \operatorname{sech}(\sqrt{Q}x)\tanh x, \quad i,j=1,2 . \end{aligned} \tag{4.13b}$$

Equations (4.13) are the linear ordinary differential equations the solutions of which are easily obtained

$$u^{(1)}_{i,j}=C^{(1)}_{i,j}P^1_1(\tanh x)+C^{(2)}_{i,j}Q^1_1(\tanh x)+\frac{(-1)^j}{2}U_{i,j} , \tag{4.14a}$$

$$\begin{aligned} U_{i,j}=&Q^1_1(\tanh x)\int P^1_1(\tanh x)\operatorname{sech}x \tanh(\sqrt{Q}x)dx\\ &-P^1_1(\tanh x)\int Q^1_1(\tanh x)\operatorname{sech}x \tanh(\sqrt{Q}x)dx , \end{aligned} \tag{4.14b}$$

$$\begin{aligned} v^{(1)}_{i,j}=&D^{(1)}_{i,j}P^1_1[\tanh(\sqrt{Q}x)]\\ &+D^{(2)}_{i,j}Q^1_1[\tanh(\sqrt{Q}x)]+\frac{(-1)^i}{2\sqrt{Q}}V_{i,j} , \end{aligned} \tag{4.14c}$$

$$\begin{aligned} V_{i,j}=&Q^1_1[\tanh(\sqrt{Q}x)]\\ &\times\int P^1_1[\tanh(\sqrt{Q}x)]\operatorname{sech}(\sqrt{Q}x)\tanh x\, dx\\ &-P^1_1[\tanh(\sqrt{Q}x)]\\ &\times\int Q^1_1[\tanh(\sqrt{Q}x)]\operatorname{sech}(\sqrt{Q}x)\tanh x\, dx ,\\ &i,j=1,2 , \end{aligned} \tag{4.14d}$$

where $P^1_1(y)$ and $Q^1_1(y)$ are the associated Legendre polynomials of first and second kind, respectively, $C^{(1)}_{i,j}$, $C^{(2)}_{i,j}$, $D^{(1)}_{i,j}$, and $D^{(2)}_{i,j}$ are constants to be determined by the boundary conditions. It is obvious that

$$\varphi_{i,j}(\pm\infty)<\infty, \quad \varphi'_{i,j}(\pm\infty)<\infty, \quad i,j=1,2 . \tag{4.15}$$

Considering Eqs. (3.14), it is reasonable to require that

$$\varphi_{1,1}(0)=\varphi_{1,2}(0)=\varphi'_{2,1}(0)=\varphi'_{2,2}(0)=\pi , \tag{4.16a}$$

$$\varphi'_{1,1}(0)=\varphi'_{1,2}(0)=\varphi_{2,1}(0)=\varphi_{2,2}(0)=0 . \tag{4.16b}$$

By using the boundary conditions Eqs. (4.15) and (4.16), the integral constants are determined as

$$C^{(1)}_{i,j}=D^{(1)}_{i,j}=0 , \tag{4.17a}$$

$$C^{(2)}_{i,j}=(-1)^j\tfrac{1}{2}\ln 2 , \tag{4.17b}$$

$$D^{(2)}_{i,j}=(-1)^i\frac{1}{2Q}(1-\ln 2), \quad i,j=1,2 , \tag{4.17c}$$

where we have used the approximations

$$\int f(x)\tanh(\sqrt{Q}x)dx\simeq\int f(x)\tanh 2x\, dx , \tag{4.18a}$$

$$\int \ln(1+\tanh^2 x)dx\simeq(x-\tanh x)\ln 2 . \tag{4.18b}$$

Then the perturbation solutions $u^{(1)}_{i,j}$ and $v^{(1)}_{i,j}$ may be written as

$$u^{(1)}_{i,j}\simeq\frac{(-1)^{j+1}}{2}\left[\operatorname{sech}x(x+\ln 2\tanh x-\tan^{-1}\tanh x)-\sinh x\ln\left[\frac{1+\tanh^2 x}{2}\right]\right] , \tag{4.19a}$$

$$v^{(1)}_{i,j}\simeq\frac{(-1)^{i+1}}{2\sqrt{Q}}\left\{\frac{1}{\sqrt{Q}}\sinh(\sqrt{Q}x)\left[1-\tanh(\sqrt{Q}x)\tanh x+\ln\left[\frac{1+\tanh^2}{2}\right]\right]+\operatorname{sech}(\sqrt{Q}x)(x-\ln 2\tanh x)\right\}, \quad i,j=1,2 . \tag{4.19b}$$

Note that

$$u^{(1)}_{i,j}(-x)=-u^{(1)}_{i,j}(x), \quad v^{(1)}_{i,j}(-x)=-v^{(1)}_{i,j}(x) ,\quad i,j=1,2 . \tag{4.20}$$

Substituting Eqs. (4.19) into (4.11) and (2.12), we obtain

$$\varphi_{i,j}=\varphi^{0}_{i,j}+\epsilon[u^{(1)}_{i,j}+(-1)^{i+1}v^{(1)}_{i,j}]/2 , \tag{4.21a}$$

$$\varphi'_{i,j}=\varphi^{0\prime}_{i,j}+\epsilon[u^{(1)}_{i,j}-(-1)^{i+1}v^{(1)}_{i,j}]/2 , \quad i,j=1,2 . \tag{4.21b}$$

Numerical calculation of Eqs. (4.21) reveals that the perturbation terms change the shape of the unperturbed solitons slightly. The energy revision for $E_{1,1}$,$E_{2,2}$ is very small and may be neglected. On the other hand, the energy of solitons $\varphi_{1,2}$ and $\varphi'_{1,2}$ (or $\varphi_{2,1}$ and $\varphi'_{2,1}$) will depend upon the length of the base pair in the case of $\lambda\neq 0$.

V. PHONON MODE

Assuming φ and φ' are small, then Eqs. (2.13) reduce to

$$u_{zz}-(1/c_0^2)u_{tt}=(1/l^2)[1+\lambda/(3\beta)]u , \tag{5.1a}$$

$$v_{zz}-(1/c_0^2)v_{tt}=(1/l^2)[Q+\lambda/(3\beta)]v . \tag{5.1b}$$

We look for the solution of Eqs. (5.1) which depends upon only a single variable ξ in the case of $c > c_0$; then Eqs. (5.1) reduce to

$$d^2u/d\xi^2 = -k_u u \ , \tag{5.2a}$$

$$d^2v/d\xi^2 = -k_v v \ , \tag{5.2b}$$

where

$$k_u^2 = k^2[1+\lambda/(3\beta)], \quad k_v^2 = k^2[Q+\lambda/(3\beta)] \ , \tag{5.3}$$

$$k^2 = (c^2/c_0^2 - 1)^{-1} l^{-2} \ . \tag{5.4}$$

The solutions of Eqs. (5.2) are

$$u = A' \cos(w_u t - k_u z + \theta') \ , \tag{5.5a}$$

$$v = B' \cos(\omega_v t - k_v z + \delta') \ , \tag{5.5b}$$

where

$$\omega_u = k_u c, \quad \omega_v = k_v c \ , \tag{5.6}$$

and A', B', θ', and δ' are constants. Assuming $A' = B'$ and $\theta' = \delta' = 0$ without losing generality, we obtain

$$\varphi = A' \cos(\omega^- t - k^- z)\cos(\omega^+ t - k^+ z) \ , \tag{5.7a}$$

$$\varphi' = A' \sin(\omega^- t - k^- z)\sin(\omega^+ t - k^+ z) \ , \tag{5.7b}$$

where

$$\omega^\pm = \sigma^\pm \omega, k^\pm = \sigma^\pm k, \omega = kc \ , \tag{5.8a}$$

$$\sigma^\pm = \frac{(Q-1)^{1/2}}{2}[(1+\sin\theta)/\cos\theta]^{\pm 1} \ , \tag{5.8b}$$

$$\sin\theta = [(3\beta+\lambda)/(2B+\beta+\lambda)]^{1/2} \ . \tag{5.8c}$$

The above solutions correspond to the motion of phonon mode of DNA chains. Substituting the solutions Eqs. (5.7) into (2.7) and (2.9), the energy per cm of phonic wave in DNA double helix is

$$E_p = \tfrac{1}{2} A'^2 (B + 2\beta + \lambda)(1-\gamma^2)/a \ . \tag{5.9}$$

It is easy to see that the dispersion relation of the phonon mode is obtained as

$$\omega^2 = \omega_0^2 + c_0^2 k^2, \quad \omega_0 = c_0/l \ , \tag{5.10}$$

which yields

$$c c_g = c_0^2 \ , \tag{5.11}$$

where c_g is the group velocity, thus we always have $c_g < c_0$.

VI. ESTIMATION OF PARAMETER VALUES AND DISCUSSIONS

There are four parameters in this theory: B, β, λ, and S. It is easy to see from Hamiltonian (2.7) that the quantities $2B$, 4β, 2λ, and $4S$ correspond to the energy of H bonds, the energy of dipole-dipole interaction, the energy of dipole—induced-dipole interaction and the stacking energy, respectively. All the energies listed above were calculated by the method of quantum chemistry.[9,14] According to Fujita *et al.*,[14] the mean stacking energy in B-form DNA is (all the parameters are in eV)

$$4S = \begin{cases} 0.15 \ (\text{CNDO method}) \\ 0.05 \ (\text{PPP method}) \end{cases} , \tag{6.1}$$

(CNDO is the complete neglect of differential overlap and PPP is Pariser-Parr-Pople). Denoting the numbers of G-C and A-T pairs in a DNA chain by $N(G\text{-}C)$ and $N(A\text{-}T)$, respectively, a factor α is defined as

$$\alpha = N(G\text{-}C)/[N(G\text{-}C)+N(A\text{-}T)] \ , \tag{6.2}$$

which is connected directly with the melting temperature of DNA double helix. In fact, the value of $B(\beta,\lambda)$ is a mean value in the sense that

$$B = (1-\alpha)B_{AT} + \alpha B_{GC} \ , \tag{6.3a}$$

$$\beta = (1-\alpha)\beta_{AT} + \alpha\beta_{GC} \ , \tag{6.3b}$$

$$\lambda = (1-\alpha)\lambda_{AT} + \alpha\lambda_{GC} \ , \tag{6.3c}$$

where $B_{AT}, \beta_{AT}, \lambda_{AT}$ and $B_{GC}, \beta_{GC}, \lambda_{GC}$ are B, β, and λ parameters corresponding to A-T and G-C base pairs, respectively. The calculation of Fujita *et al.* reported that the H-bond energies in the B-form DNA were (in eV) 0.48 (CNDO) and 0.39 (PPP) for the G-C base pair, and 0.076 (CNDO) and 0.070 (PPP) for the A-T base pair. On the other hand, for the DNA chains taken from many types of living beings, $\alpha \simeq 0.4$. Substituting the above results into Eq. (6.3a), we obtain

$$B = \begin{cases} 1.2 \times 10^{-1} \ (\text{CNDO}) \\ 1.0 \times 10^{-1} \ (\text{PPP}) \ . \end{cases} \tag{6.4}$$

Now we shall use formula (2.4) to determine the parameter β. According to Devoe and Tinoco[9] we have (μ in D)

$$\mu_A = 2.8, \quad \mu_G = 6.9, \quad \mu_T = 3.5, \quad \mu_C = 8.0, \quad R = 6.4\ \text{Å} \ , \tag{6.5}$$

and substituting Eqs. (6.5) into (2.4) and (6.3b), considering that $\beta_{GC} > 0$ (head-to-tail arrangement), $\beta_{AT} < 0$ (head-to-head arrangement), we obtain

$$\beta = 3.9 \times 10^{-2} \ . \tag{6.6}$$

The interaction energy of dipole-induced—dipole between two bases G-C or A-T was calculated by Devoe and Tinoco, also. They reported that

$$2\lambda_{GC} = 1.3 \times 10^{-2}, \quad 2\lambda_{AT} = 4.3 \times 10^{-3} \ . \tag{6.7}$$

Substituting the above results into Eq. (6.3c), we obtain

$$\lambda = 4.0 \times 10^{-3} \ . \tag{6.8}$$

Then all the four parameters are determined. Therefore we have

$$Q = \frac{2B+\beta}{3\beta} = \begin{cases} 2.4 \ (\text{CNDO}) \\ 2.1 \ (\text{PPP}) \ , \end{cases} \tag{6.9}$$

$$\epsilon = 2\lambda/(3\beta) = 0.068 \ . \tag{6.10}$$

In this theory the 2π soliton Eq. (4.3) has the lowest energy. Therefore it is reasonable to assume that only these solitons are excited in the condition of solvent to take part in the H-D exchange reaction, then our theory predicts the enthalpy difference ΔH of open and closed forms by using Eq. (4.5) and the determined parameters as (in kcal per mole)

$$\Delta H = \begin{cases} 13.4 \text{ (CNDO)} \\ 7.7 \text{ (PPP)} . \end{cases} \tag{6.11}$$

Nakanishi and Tsuboi reported that the experimental value was 8.1.[3] So our result is in agreement with this in order of magnitude.

It is believed that the DNA solitons may be excited by some chemical reactions in the biological process so that the soliton excitations will be interesting and promising physiologically in the explanation of the duplication of DNA and the transcription of mRNA. Although the soliton excitations in DNA chains may be important, however, the existence of these solitons is still an unresolved problem.

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